



Short communication

## A simple and inexpensive synthesis route for LiFePO<sub>4</sub>/C nanoparticles by co-precipitation

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### HIGHLIGHTS

- A one-step co-precipitation process with ethylene glycol was applied.
- We found out a convenient route to synthesize nanoscale LiFePO<sub>4</sub>/C composites.
- The composites with uniform carbon coating performed excellently in electrochemical test.
- This method can reduce cost and is expected to have efficient commercial application.

### ARTICLE INFO

Article history:

Received 2 July 2012

Received in revised form

15 January 2013

Accepted 19 January 2013

Available online 28 January 2013

### ABSTRACT

A one-step co-precipitation process with ethylene glycol in aqueous solution was carried out to provide a convenient and economic route for the synthesis of nanoscale LiFePO<sub>4</sub>/C composites with uniform carbon coating and excellent electrochemical performance. It can be easily scaled up for commercialization.

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Keywords:

Lithium iron phosphate

Co-precipitation

Nanoparticles

Carbon coating

### 1. Introduction

Nowadays, the demand for high-performance rechargeable lithium-ion batteries is dramatically increasing. Because of the significant impacts on the performance, cost and safety of battery, the cathode material has attracted the most attention among the components in lithium-ion batteries [1]. LiFePO<sub>4</sub> is one of the most promising candidates for cathode materials of lithium ion batteries owing to its excellent cycle life, inexpensiveness, remarkable thermal stability and nontoxicity [2]. However, the low electronic and ionic conductivities limit its application in high power density batteries. Therefore, various approaches have been used to improve the performance of LiFePO<sub>4</sub>, such as carbon coating [1,3–5], metal doping [6,7] and downsizing the particles [8,9]. In particular, carbon coating has been widely used for enhancing the specific capacity and rate capacity. The carbon coating around the particles not only improves the electronic conductivities, but also suppresses particle growth and

sintering. The as-prepared small particles can shorten the distance of lithium ion diffusion in solid-state phase, and further enhance the ion conductivity which leads to better electrochemical performance. LiFePO<sub>4</sub> can be synthesized by many chemical methods, such as solid state reaction [10], hydrothermal method [11,12], sol–gel technique [13,14], co-precipitation [8,15,16], etc. Among these methods, the co-precipitation route for synthesizing LiFePO<sub>4</sub>/C nanoparticles offers more advantages such as the comparatively homogeneous mixing of starting material at molecular level, convenient synthesis process and less energy consumption.

In this work, we report a simple and inexpensive co-precipitation method for preparation of nano-sized LiFePO<sub>4</sub>/C particles with excellent electrochemical properties. Although we used ferrous sulfate as raw material, all procedures of the co-precipitation process were operated in ambient environment without gas protection. It can be easily scaled up for commercialization.

### 2. Experimental

LiFePO<sub>4</sub>/C nanoparticles were prepared by a co-precipitation method at room temperature. FeSO<sub>4</sub>·7H<sub>2</sub>O and H<sub>3</sub>PO<sub>4</sub> (85%) were

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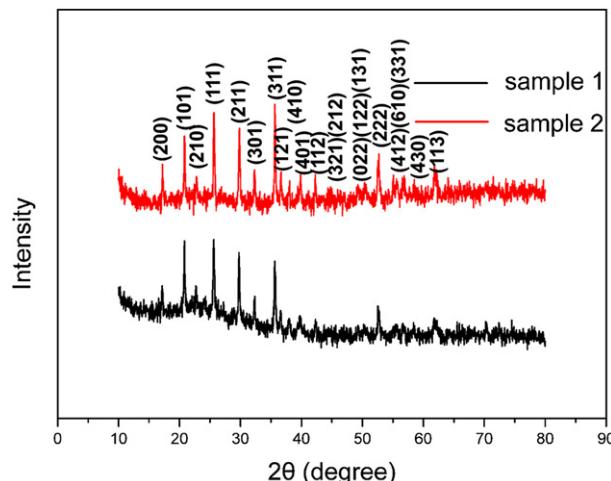
dissolved in 10 mL of de-ionized water. Then 20 mL ethylene glycol (sample 1) or 20 mL de-ionized water (sample 2) were added to the solution. Next, a 20 mL aqueous solution of LiOH was put into the acquired solution under vigorous stirring. The molar ratio of Li/Fe/P is 3:1:1. After 2 h stirring, the solutions were filtered to obtain the precipitate precursors. The filtrate can go on to be recycled as the source of lithium ion and ethylene glycol. The co-precipitate was washed several times with de-ionized water, and then mixed with a glucose solution which was used as carbon source. This mixture was stirred at 80 °C to remove the excess water. The final precursor was firstly heated to 250 °C for 5 h and then calcined at 650 °C for 10 h in a tubular furnace under an Ar/H<sub>2</sub> (95/5 vol%) gas flow.

XRD measurements were carried out with a Bruker D8-Advance powder X-ray diffractometer with Cu-K $\alpha$  radiation. The morphology and nanostructure of the products were characterized using a transmission electron microscope (TEM, JEM-2100) and a scanning electron microscope (QUANTA-FEG-250). The specific surface areas were examined by nitrogen adsorption–desorption isotherms at 77 K via the Brunauer–Emmet–Teller (BET) method. The instrument employed was a QuadraSorb SI system. The residual carbon amount is 8%, which was measured by elemental analyser (Vario EI III, Elementar Analysen System GmbH, Germany).

The electrochemical properties of the samples were characterized using CR2032 coin cells. The coin cells were prepared with LiFePO<sub>4</sub>/C cathode, metallic lithium anode, 1 M LiPF<sub>6</sub> in a mixture of ethylene carbonate (EC), diethyl carbonate (DEC) and ethyl methyl carbonate (EMC) (1:1:1 in volume ratio) as electrolyte and microporous polypropylene as separator. The cells were assembled in an Ar-filled dry glove-box. The cathodes were fabricated by dispersing the active material, conductive carbon (super P) and poly(vinylidene fluoride) (PVDF) binder at a weight ratio of 80:10:10 in N-methyl-2-pyrrolidone (NMP). After casted with the mixture uniformly, an aluminum foil was dried in vacuum at 100 °C for 12 h. Then individual electrodes ( $\varnothing = 12$  mm) were punched out. Active material loading is 1–2 mg. The charge–discharge testing was performed at different C rates between 2.5 and 4.2 V on a LAND CT-2000A cell test instrument at room temperature.

### 3. Results and discussion

**Fig. 1** shows the XRD patterns of the two samples after calcination. All the intense diffraction peaks of the two samples could be well

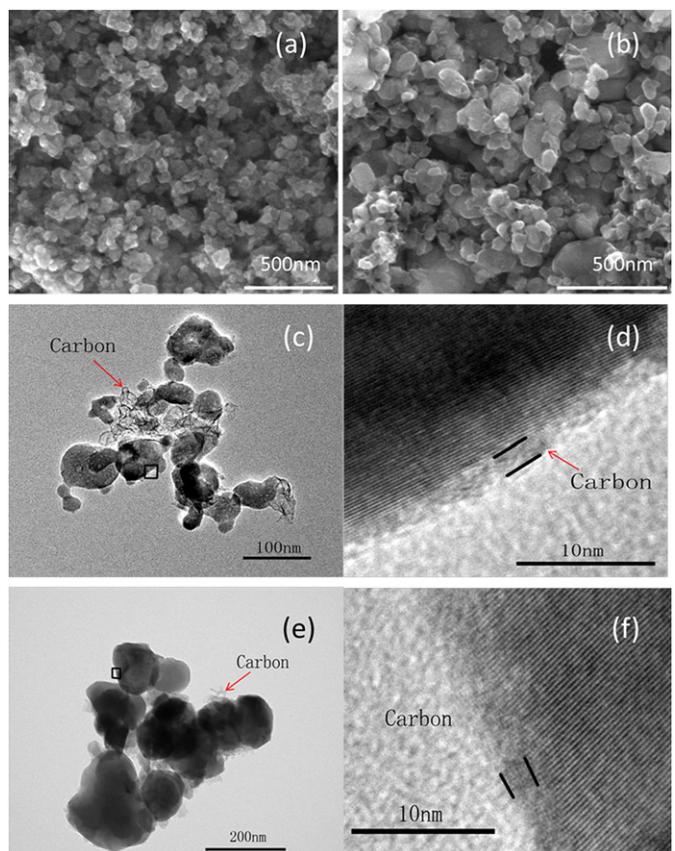


**Fig. 1.** XRD patterns of sample 1 (black) and sample 2 (red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

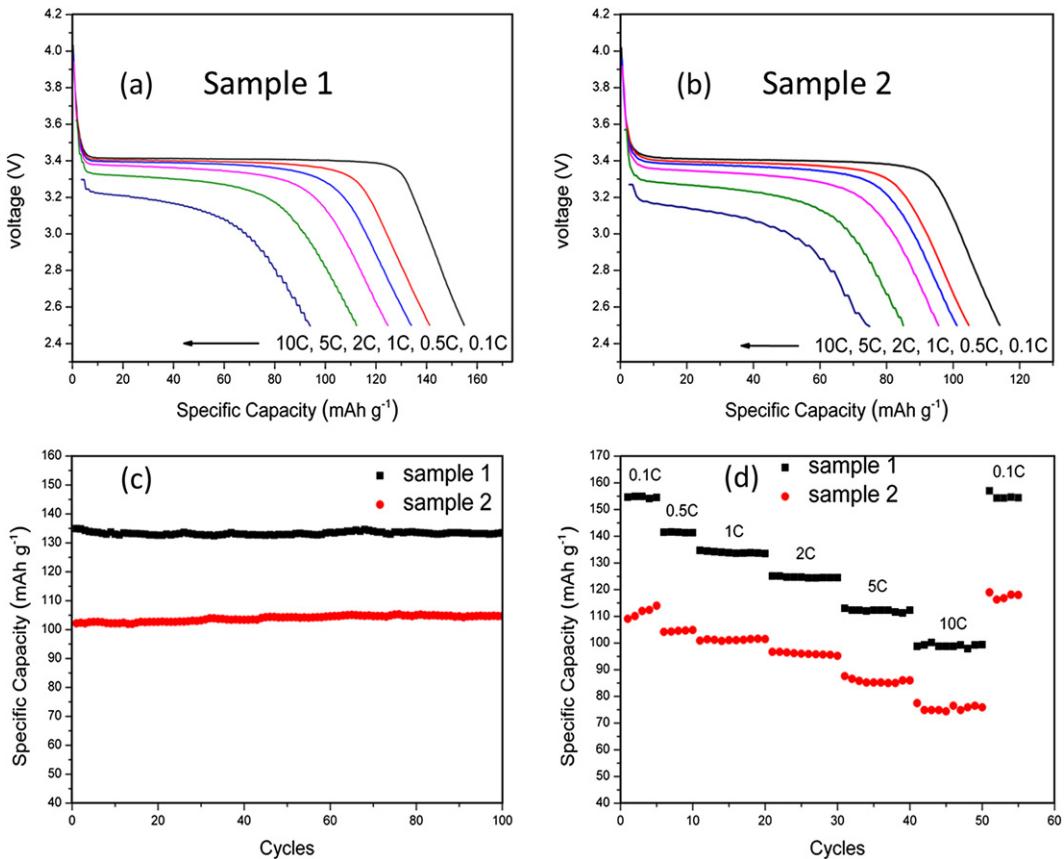
indexed to the orthorhombic olivine-type structure with the Pnma space group. The XRD patterns show a pure LiFePO<sub>4</sub> phase without any obvious evidence of other phases or impurities. There are no noticeable diffraction peaks corresponding to the residual carbon, indicating that the carbon in the sample is in amorphous state.

Ethylene glycol was put in to control particle size and homogenize the LiFePO<sub>4</sub>/C nanoparticles. It worked as a thickening agent, which increased the viscosity of the system. Thus, we could control the precipitate growth rate and prevent precipitate from growing bigger. It could also prevent the oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup>. The images from scanning and transmission electron microscopes (**Fig. 2**) support our opinion. In **Fig. 2(a)**, sample 1 exhibits a uniform particle size distribution, and the average particle size is around 50 nm while sample 2 has a larger particle size distribution (80–200 nm) (**Fig. 2(b)**). The small particle size can facilitate the delithiation and lithiation processes and enhance the electrochemical properties of LiFePO<sub>4</sub>. As for TEM images, **Fig. 2(c)** exhibits that the particles of sample 1 are 30–80 nm in diameter, which agrees with the SEM result. **Fig. 2(e)** also confirms the results of sample 2 in SEM image.

The TEM images (**Fig. 2c–f**) clearly reveal that each particle is completely coated by a carbon layer to form a LiFePO<sub>4</sub>/carbon core–shell structure. In **Fig. 2(d and f)**, the HRTEM images corresponding to the selected areas marked by a rectangle in **Fig. 2(c and e)** are shown. A uniform amorphous carbon film with thickness of about 2 nm on the particle surface is observed. The intercalation/deintercalation of lithium ion through the carbon shell is easy because of the thin carbon film, and this carbon film is also helpful to promote electron conductivity. Such uniform and integrated carbon shell may be due to the pre-sintering process at 250 °C for 5 h. At 250 °C, the glucose began to decompose, and the following calcination made the decomposed product carbonize. At the same time,



**Fig. 2.** Electron microscopy images of the two samples after calcination. SEM images: (a) sample 1, (b) sample 2. TEM images: (c and d) sample 1, (e and f) sample 2.



**Fig. 3.** Electrochemical properties. (a and b) Typical discharge curves of sample 1 and 2 at various rates. (c) Cycle performances at 1C discharge rate. (d) Discharge capacities at various charge–discharge C-rates as indicated in the range 2.5–4.2 V (vs. Li/Li<sup>+</sup>).

LiFePO<sub>4</sub> crystals were formed. Therefore, the carbon can coat on the LiFePO<sub>4</sub> particles uniformly and entirely.

The surface area of the sample 1 is 54.626 m<sup>2</sup> g<sup>-1</sup>, and that of sample 2 is 59.224 m<sup>2</sup> g<sup>-1</sup>. They are larger than those of LiFePO<sub>4</sub> synthesized by Doherty et al. [17], Yim et al. [18] and Wang et al. [19]. The large surface area is attributed to both the construction of carbon nano-interconnect among the LiFePO<sub>4</sub> grains and the small particle size. It can stimulate the active material to make a full contact with the electrolyte, which in turn leads to easier lithium ion diffusion between them.

Electrochemical properties of the two samples were studied by measuring the charge–discharge profiles and cyclic performance. In Fig. 3(a and b), the discharge curves of the two samples at 0.1 C have a long flat potential plateau at around 3.4 V, which indicates that the two-phase redox reaction proceeds via a first-order transition between LiFePO<sub>4</sub> and FePO<sub>4</sub> [2]. Sample 1 at 0.1 C delivers a discharge capacity of 155 mAh g<sup>-1</sup>, which is close to the theoretical capacity of 170 mAh g<sup>-1</sup> (Fig. 3a)[2]. As shown in Fig. 3b, the discharge capacity of sample 2 is 120 mAh g<sup>-1</sup> at 0.1 C, which is smaller than that of the sample 1. The discharge curves at various C-rates are also shown. They display that the flat potential plateaus are shorter and inclined to drop in potential dominate. The plateau potential drops are 0.2 V (=3.4–3.2 V) (sample 1) and 0.3 V (=3.4–3.1 V) (sample 2) at 0.1 C–10 C. Diffusion polarization at high discharge C-rate brings this outcome. It means that the mass transport step of lithium ion is slower than other steps in the electrochemical reaction. Sample 1 has the smaller plateau potential drop because of the smaller particle size. Small particle has short transport path, which can accelerate lithium ion diffusion to reduce polarization at high discharge C-rate. Fig. 3c presents the extraordinary cyclic performance of the two

samples at 1 C. The discharge capacities of the two samples are 134 mAh g<sup>-1</sup> (sample 1) and 104 mAh g<sup>-1</sup> (sample 2). It can be seen that there is no obvious capacity fading after 100 cycles at 1 C. More than that, after several circles, the capacity of sample 2 even increases a little which is owing to more exposure of LiFePO<sub>4</sub>/C to electrolyte. Fig. 3d exhibits excellent rate behavior. The discharge capacity of sample 1 remains at 100 mAh g<sup>-1</sup> even at a high rate of 10 C, which is due to the small and homogeneous particle size. And the discharge capacity of sample 2 is only 75 mAh g<sup>-1</sup>. Invisible discharge capacity fading of the samples has been found after 10 cycles at each high rate. Furthermore, the discharge capacity of the two samples can be totally recovered when the discharge rate reduces from 10 C to 0.1 C, which indicates extraordinarily high cycling stability after a large number of high rates cycles. These results can meet the requirement of tolerating various discharge currents and long cycle life for high power applications.

#### 4. Conclusions

In summary, a simple co-precipitation preparation technique, which avoided expensive chemicals and particular equipment, was applied to produce nano-sized LiFePO<sub>4</sub>/C particles with uniform carbon coating. The composites have excellent cycling and rate performance, which meet the demand of high power batteries.

#### Acknowledgments

This work was supported by the Natural Science Foundation of China (21076115) and the National 973 Basic Research Program of China (No. 2011CB935901).

**References**

- [1] J.J. Wang, X.L. Sun, *Energy Environ. Sci.* 5 (2012) 5163.
- [2] A.K. Padhi, K.S. Nanjundaswamy, J.B. Goodenough, *J. Electrochem. Soc.* 144 (1997) 1188.
- [3] N. Ravet, J.B. Goodenough, S. Besner, M. Simoneau, P. Hovington, M. Armand, Abstract 127, The Electrochemical Society and The Electrochemical Society of Japan Meeting Abstracts, vol. 99-2, Honolulu, HI, Oct. 17–22, 1999.
- [4] H. Huang, S.C. Yin, L.F. Nazar, *Electrochem. Solid-State Lett.* 4 (2001) A170.
- [5] J.P. Zhou, J.P. Tu, L.J. Cheng, S.J. Shi, Y.Q. Qiao, W.L. Liu, X.L. Wang, C.D. Gu, *J. Electrochem. Soc.* 158 (2011) A1237.
- [6] N. Ravet, A. Abouimrane, M. Armand, *Nat. Mater.* 2 (2003) 702.
- [7] S.Y. Chung, Y.M. Chiang, *Electrochem. Solid-State Lett.* 6 (2003) A278.
- [8] C. Delacourt, P. Poizot, S. Levasseur, C. Masquelier, *Electrochem. Solid-State Lett.* 9 (2006) A352.
- [9] A. Yamada, S.C. Chung, K. Hinokuma, *J. Electrochem. Soc.* 148 (2001) A224.
- [10] L. Kavan, I. Exnar, J. Cech, M. Graetzel, *Chem. Mater.* 19 (2007) 4716.
- [11] Y.H. Lu, J.B. Goodenough, Y. Kim, *J. Am. Chem. Soc.* 133 (2011) 5756.
- [12] M.H. Lee, J.Y. Kim, H.K. Song, *Chem. Commun.* 46 (2010) 6795.
- [13] Y.S. Hu, Y.G. Guo, R. Dominko, M. Gaberscek, J. Jamnik, J. Maier, *Adv. Mater.* 19 (2007) 1963.
- [14] Y.K. Zhou, J. Wang, Y.Y. Hu, R. O'Hare, Z.P. Shao, *Chem. Commun.* 46 (2010) 7151.
- [15] S.W. Oh, S.T. Myung, S.M. Oh, K.H. Oh, K. Amine, B. Scrosati, Y.K. Sun, *Adv. Mater.* 22 (2010) 4842.
- [16] P. Gibot, M. Casas-Cabanas, L. Laffont, S. Levasseur, P. Carlach, S. Hamelet, J.M. Tarascon, C. Masquelier, *Nat. Mater.* 7 (2008) 741.
- [17] C.M. Doherty, R.A. Caruso, B.M. Smarsly, C.J. Drummond, *Chem. Mater.* 21 (2009) 2895.
- [18] C.H. Yim, E.A. Baranova, Y. Abu-Lebdeh, I. Davidson, *J. Power Sources* 205 (2012) 414.
- [19] Y.G. Wang, Y.R. Wang, E. Hosono, K.X. Wang, H. Zhou, *Angew. Chem. Int. Ed.* 47 (2008) 7461.